Emission spectroscopic determination of B and Cd in magnesium used in uranium production

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Abstract. An emission spectroscopic method was developed for the determination of B and Cd at trace levels in magnesium employed in the production of nuclear-grade uranium. Magnesium sample was converted to magnesium oxide and ground with pure conducting graphite powder containing LiF and Ga_2O_3. Thirty mg of the mixture was excited in a DC arc operated at 12 A. A polychromator having secondary slits for B and Cd at 249·77 nm and 228·80 nm respectively was used for recording the intensities. The method gave a mean relative standard deviation of 5·5% for B and 7·6% for Cd in the concentration range 1–10 ppm.

Keywords. Boron; cadmium; emission spectroscopy; magnesium oxide; trace elements.

1. Introduction

Nuclear-grade uranium is prepared by magnesio-thermic reduction of high-purity uranium tetrafluoride. Uranium thus produced should not contain B and Cd (nuclear poisons) at more than 0·1 ppm each. Although high-purity UF_4 is employed in the reduction process, the purity of uranium metal will also depend on the purity of the magnesium metal. It is therefore necessary to determine the purity of the magnesium metal, especially with respect to the presence of B and Cd. The possibility of uranium picking up B and Cd from magnesium is more if the latter contains > 1 ppm each of these elements. Optical emission spectroscopy (OES) is a convenient technique for the determination of traces of B and Cd in magnesium, because it is both rapid and sensitive. However, the analysis is done after converting the metal to its oxide (MgO), since it is difficult to have calibration standards containing B and Cd at trace levels in the magnesium metal. In the past, many workers (Degtyareva *et al* 1962; Pevtsov *et al* 1969; Krishnamurty *et al* 1973; Capdevila and Diaz-Guerra 1979; Murty *et al* 1983) employed the OES technique for the determination of some trace elements in MgO. All these workers used DC arc excitation and photographic detection and reported detection limits of 1 and 5 ppm respectively for B and Cd. We developed an OES method using DC arc excitation to estimate B and Cd with a detection limit of 1 ppm each in Mg metal, after conversion to MgO. We employed photoelectric detection to obtain the signals corresponding to the analytical lines of B and Cd. Hence it was necessary to apply background correction. An on-line background correction procedure was evolved to determine net peak signals.

2. Experimental

2.1 *Preparation of standards*

A master standard containing 5000 ppm each of B and Cd in MgO was prepared by grinding together appropriate quantities of 'Specpure'-grade B metal and CdO (obtained from Johnson Matthey & Co.). The matrix MgO was also of Specpure grade. The master standard was successively diluted with Specpure-grade MgO to obtain a set of four calibration standards in which B and Cd were present at 1, 2, 5 and 10 ppm. A buffer mixture was prepared separately by grinding pure graphite powder, LiF and Ga_2O_3 in the ratio 45:4:1 by weight. Gallium was added as Ga_2O_3 to serve as internal standard. Each calibration standard was ground with the buffer mixture in the ratio 4:1 by weight. A blank containing only MgO and the buffer mixture was also prepared.

2.2 *Preparation of samples*

Magnesium metal samples received in the form of granules were pickled in dilute HNO_3, washed with distilled deionized water and dried. One hundred mg of each sample was taken in a platinum dish and dissolved in 1:1 (v/v) HNO_3 (electronic grade). The magnesium nitrate solution thus obtained was slowly evaporated by keeping the platinum dish on a sand bath. The dried magnesium nitrate in the form of crystals was ignited in a furnace, set at 600°C for 2 h, to obtain MgO. Each sample after conversion to oxide was ground with the buffer mixture in the ratio 4:1 by weight.

2.3 *On-line background correction procedure*

The instrumentation used and relevant experimental conditions are given in table 1. The spectrometric procedure involves the measurement of background-corrected peak

Table 1. Experimental details.

Spectrometer	Jobin-Yvon Model JY-48 polychromator with 1 metre concave grating
Grating grooves	2550 per mm
Wavelength range	130–415 nm in I order
Reciprocal linear dispersion	0·39 nm/mm in I order
Location of secondary slits (channels)	B 249·77 nm, Cd 228·80 nm, Ga 241·87 nm, reference channel 243·2 nm
Lower electrode (anode)	UCC type 100-L graphite electrode with reduced cavity to accommodate 30 mg standard/sample
Upper electrode (cathode)	4·76 mm dia. UCC pointed graphite electrode
Excitation source	DC operated at 12 A and 230 V
Integration time	40 seconds (divided into 10 equal segments)
Data acquisition system	Apple IIe

intensities for B, Cd and Ga in both standards and samples. The scheme for obtaining net peak intensities from the recorded signals of B, Cd and Ga is outlined below. Two blank (MgO + buffer) charges were arced at two positions of the primary slit such that these corresponded to the background positions on either side of the analyte line peak. The signals for B, Cd, Ga and a reference channel were recorded for both positions of the primary slit. Background factors (background signal of the analyte/ signal at the reference channel) were then calculated at both the above positions. From these data the average background factors for B, Cd and Ga were determined. Calibration standards and samples were arced with the primary slit set at normal profile position (micrometer reading) where secondary slits of B, Cd and Ga would receive maximum signals. Using the signal at the reference channel and the average background factors for B, Cd and Ga the background intensities were obtained. These intensities were substracted from the peak intensities to get net peak intensities (I_B, I_{Cd}, I_{Ga}). The calibration plots for B and Cd were obtained by plotting (I_B/I_{Ga}) vs concentration and (I_{Cd}/I_{Ga}) vs concentration on logarithmic scale.

3. Results and discussion

3.1 *Choice of thermochemical additive*

In DC arc OES, addition of certain compounds or substances to the sample is known to increase the volatilization of the analytes and hence enhance their line intensities. These compounds are called thermochemical additives. Some halides are known to serve as thermochemical additives very efficiently. In the present case three compounds, viz. LiF, NaF and NH_4Cl, were tried. Three sets of calibration standards, each having B and Cd in the concentration range 1–10 ppm, were prepared. Each set was independently ground with 2% each of LiF, NaF and NH_4Cl. In each case the intensity ratios of B and Cd with respect to Ga (internal standard) were determined for each calibration standard. The data are given in table 2. It is seen from these data that the addition of NaF yielded higher intensity ratios for both B and Cd. With NH_4Cl the intensity ratios B/Ga were higher than those obtained with LiF. However, it was observed that in the presence of LiF, the MgO standards or samples volatilized smoothly without arc wandering. Since smooth volatilization was necessary to attain good precision, LiF was chosen as the thermochemical additive. For 1 ppm standard relative standard deviation was 5·8% for B with LiF while it was 20% with NH_4Cl.

Table 2. Intensity ratios with LiF, NaF and NH_4Cl additives.

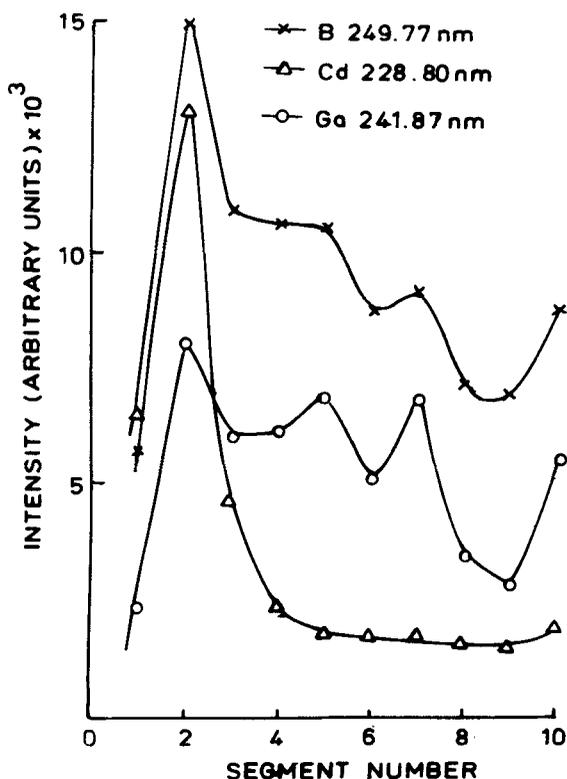| Concentration of B or Cd (ppm)	Intensity ratio: B/Ga			Intensity ratio: Cd/Ga		
	LiF	NaF	NH_4Cl	LiF	NaF	NH_4Cl
1	0·19	0·27	0·28	0·17	0·23	0·17
2	0·31	0·39	0·35	0·25	0·30	0·28
5	0·55	0·60	0·72	0·43	0·58	0·47
10	0·95	1·22	1·26	0·56	0·77	0·57

Figure 1.   Volatilization of B, Cd and Ga in MgO.

3.2   *Choice of internal standard*

Gallium, which is not normally present in Mg samples, was added as Ga_2O_3 to serve as the internal standard. In figure 1 the volatilization behaviour of B, Cd and Ga in MgO matrix under the experimental conditions given in table 1 is shown. Intensities of B, Cd and Ga lines were recorded for each segment (4 sec) during the total integration time of 40 sec. It is seen from figure 1 that all the three elements have their maximum (peak) emission at the end of the second segment. However, B and Ga exhibit an oscillatory nature of emission, both giving appreciable intensity even after the second segment. To avail maximum contribution to the line intensity with minimum contribution from background intensity, signal acquired within the segments 1–8 was used for B and Ga. In the case of Cd the signal acquired within the segments 1–6 only was used since intensity in segments 7 and 8 was mainly due to background emission.

3.3   *Calibration with and without background correction*

The calibration plots made for B and Cd in the concentration range 1–10 ppm are shown in figures 2 and 3. The plots were made for two sets of intensity ratios. One
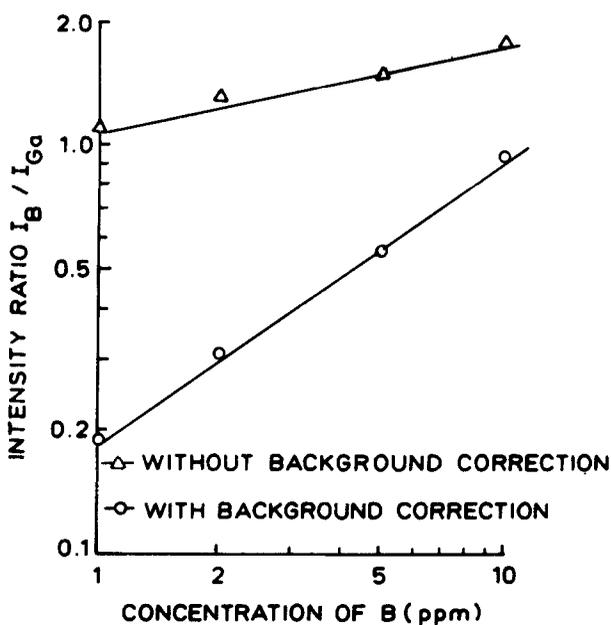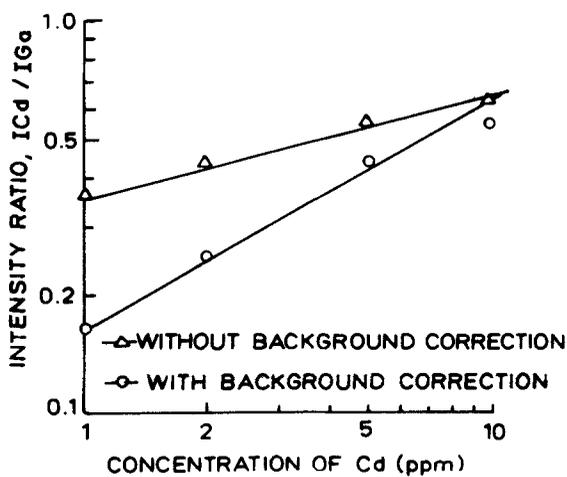
Figure 2. Calibration plot for B in MgO.

Figure 3. Calibration plot for Cd in MgO.

set of the intensity ratios was obtained without background correction and the second set with background correction. For both B and Cd the calibration plots, although linear, are very flat in appearance when background correction is not applied. On the other hand, with background corrected intensities the plots are linear with good slope.

3.4   *Precision*

The relative standard deviation (RSD) which represents the precision of the method was calculated for the .1 and 10 ppm calibration standards. The RSD was calculated by employing six intensity ratios of B and Cd corresponding to 1 and 10 ppm. The RSD values at 1 ppm level for B and Cd were 5·8% and 8·6% respectively. At 10 ppm level the RSD for B was 5·3% and that for Cd 6·6%. These values indicate that the precision of the present method is very good, considering the fact that DC arc excitation was employed.

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